Comparison of Experimental and Model Data for the Evaporation of a Synthetic Topopah Spring Tuff Pore Water, Yucca Mountain, NV

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Evaporative Evolution of Carbonate-Rich Brines from Synthetic Topopah Spring Tuff Pore Water, Yucca Mountain, NV

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ABSTRACT

The evaporation of a range of synthetic pore water solutions representative of the potential high-level-nuclear-waste repository at Yucca Mountain, NV is being investigated. The motivation of this work is to understand and predict the range of brine compositions that may contact the waste containers from evaporation of pore waters, because these brines could form corrosive thin films on the containers and impact their long-term integrity. A relatively complex synthetic Topopah Spring Tuff pore water was progressively concentrated by evaporation in a closed vessel, heated to 95ºC in a series of sequential experiments. Periodic samples of the evaporating solution were taken to determine the evolving water chemistry. According to chemical divide theory at 25ºC and 95ºC our starting solution should evolve towards a high pH carbonate brine. Results at 95ºC show that this solution evolves towards a complex brine that contains about 99 mol% Na^+ for the cations, and 71 mol% Cl^-, 18 mol% $\Sigma CO_2(aq)$, 9 mol% SO_4^{2-} for the anions. Initial modeling of the evaporating solution indicates precipitation of aragonite, halite, silica, sulfate and fluoride phases. The experiments have been used to benchmark the use of the EQ3/6 geochemical code in predicting the evolution of carbonate-rich brines during evaporation.

INTRODUCTION

Yucca Mountain, NV is the designated site for a permanent geologic repository for high-level nuclear waste. The current waste package design consists of a double walled container with an inner barrier of stainless steel, an outer barrier of highly resistant nickel-chromium-molybdenum alloy, and a titanium drip-shield that covers the containers. Corrosion resistance and long-term integrity of the metal containers and shields are important for the safe disposal of the waste. If the site is licensed, the waste packages will be placed in tunnels several hundred meters below the ground surface in partially saturated volcanic tuff. Once the waste packages are in place, the repository will heat up due to the thermal energy of the nuclear waste. Although the waste packages will be above the groundwater table, pore water present in rock formations within (Topopah Spring Tuff) and above (Paintbrush) the repository may come in contact with the metal containers and shields.

The chemical divide theory generally describes the chemical evolution of dilute waters upon evaporation in terms of their equivalent calcium, sulfate and bicarbonate mole ratios [1]. The chemical evolution of the water after significant evaporation is controlled by the high solubility of salt minerals (for example halite) relative to the moderate solubility of calcium sulfate and low solubility of calcium carbonate minerals. An alkaline pH, bicarbonate brine (Na-K-CO$_3$-Cl-SO$_4$-NO$_3$) forms from dilute waters with dissolved calcium concentrations that are less than dissolved carbonate (Ca < HCO$_3$+CO$_3$, equivalent %). A near neutral pH, sulfate brine (Na-K-Mg-Cl-SO$_4$-NO$_3$) forms from dilute waters with dissolved calcium concentrations that are greater than the dissolved carbonate, but less than the combined dissolved sulfate and carbonate concentrations (Ca < SO$_4$+HCO$_3$, equivalent %). A calcium chloride brine with near neutral pH

(Na-K-Ca-Mg-Cl-NO$_3$) forms from dilute waters with a dissolved calcium concentration that is greater than the combined dissolved sulfate and carbonate concentrations (Ca > SO$_4$+HCO$_3$, equivalent %). The measured compositions of Yucca Mountain pore water vary, but can be generally classified as waters that should evolve towards sulfate and sodium bicarbonate type brines, with a few calcium chloride brines as they evaporate.

In this study we focus on carbonate brines formed by the evaporation of pore water at elevated temperature. This study provides additional benchmark data needed to both understand the brines and salts that form upon evaporation of varied waters and to validate the EQ3/6 geochemical code and a high temperature Pitzer parameter thermodynamic database currently used by the Yucca Mountain Program to model aqueous chemical systems.

EXPERIMENTAL

A synthetic pore water solution was evaporated to approximately 2100x with respect to its initial concentration (based on potassium and nitrate conservative evaporation) at 95ºC in a series of two experiments to iteratively concentrate the solution in manageable quantities of approximately 3 liters and to monitor precipitation. The initial compositions of the evaporation legs are shown in Table 1.

Leg 1	HCO$_3^-$	Ca^{2+}	Mg^{2+}	SiO$_2$(aq)	Na$^+$	K$^+$	Sr^{2+}
millimolal	0.4214	0.169	0.033	0.278	5.413	0.063	0.005
	Br$^-$	Cl$^-$	As	NO$_3^-$	SO$_4^{2-}$	F$^-$	pH
millimolal	0.001	4.240	0	0.056	0.538	0.124	9.69

Leg 2	HCO$_3^-$	Ca^{2+}	Mg^{2+}	SiO$_2$(aq)	Na$^+$	K$^+$	Sr^{2+}
millimolal	3.789	0	0.104	0.259	247.5482	3.284	0
	Br$^-$	Cl$^-$	As	NO$_3^-$	SO$_4^{2-}$	F$^-$	pH
millimolal	0.092	188.142	0.0001	2.413	23.212	0.997	9.75

Table 1. Carbonate-rich brine starting solution compositions

The chemical composition of the second leg was based on the brine composition towards the end of the first leg. The solutions were prepared at room temperature using analytical grade salts. Differences between the ending and starting compositions for each leg reflect the difficulty in exactly synthesizing the solutions and changes that occur when the solution is prepared at 25ºC and then heated to the experimental temperature of 95ºC. Tuff was added to the solution in each leg to simulate short-term water-tuff interaction at 95ºC.

Evaporation was conducted in a vented HALAR$^{®}$-lined vessel heated to 95ºC in a fluidized sand bath furnace. The solution was stirred constantly and HEPA filtered air was streamed over the solution to help control the evaporation rate. The solution was refluxed to prevent evaporation as it was heated to run temperature. Once the solution was at 95ºC, the evolving water vapor was condensed to monitor the extent of evaporation. As the evaporation proceeded, the 3-liter volume was kept constant by the automated addition of starting solution; thus concentrating the solution at a constant volume. Periodic small-volume samples of the concentrating solution were filtered at 95ºC and analyzed to determine the water chemistry throughout the evaporation / concentration process. Sample volumes withdrawn were automatically replenished with fresh starting solution. The 95ºC filtered samples withdrawn for

cation and anion analysis were immediately diluted by directly injecting the sample into a known quantity of deionized water to prevent precipitation on cooling. Dissolved calcium, magnesium, silica, and sodium were measured with an inductively coupled plasma-atomic emission spectrometer, dissolved potassium was measured using an atomic absorption spectrophotometer, and fluoride, chloride, nitrate, and sulfate anions were determined using ion chromatography. Reproducibility of these techniques is typically better than ±2%.

Undiluted samples for infrared total dissolved inorganic carbon analysis, $\sum CO_2(aq)$, were immediately stored in filled gas tight vials to prevent equilibration with air at room temperature. Solution pH was measured from undiluted samples as soon as they cooled to room temperature. Periodic samples of the condensed water vapor were also analyzed to monitor gas volatility. After the last sample was taken for each leg, the evaporation was continued to dryness. The solid precipitate was collected at the end of each leg of the experiment and dried in an oven at 40ºC to facilitate sample preparation. Mineralogy was determined by powdered X-ray diffraction (XRD) using a Cu-K-α source from 10° to 90° 2-theta at 0.02º per step. Mineral identification was based on the presence of the three most intense peaks in the XRD pattern for a given mineral. In some cases where the most intense peaks overlapped with other mineral peaks, identification was based on the presence of lower intensity diagnostic peaks.

THERMODYNAMIC MODELING

Solution compositions were modeled using EQ3/6 geochemical code including a high temperature Pitzer ion-interaction database [2]. The high temperature Pitzer ion-interaction model approximates non-ideal behavior of solutions at elevated ionic strength and temperature. The Yucca Mountain Project high temperature Pitzer ion interaction database is the most comprehensive database available to account for the non-ideal behavior of highly concentrated electrolytes over a wide range of temperature (0 to 250ºC). The database was founded on the original variable-temperature Pitzer parameters outlined by Møller [3], supplemented by parameter data from several other sources. It also includes thermodynamic parameters converted from non-standard Pitzer equations from the published literature [4]. Temperature independent parameters based on 25ºC data [5] are used for several parameters where temperature dependent data are lacking. The database contains temperature dependent ion interaction parameters for most ion groups relevant to our experimental system at 95ºC. Exceptions include: single-temperature parameters for potassium nitrate, some calcium ion pairs and several magnesium ion pairs [5], and parameters for bicarbonate ion groups based on data from 25 to 90ºC [6]. No kinetic factors were considered in this model.

The predictive models were generated to mirror the experimental design and analysis, in which synthetic pore water was evaporated during two sequential experiments, with a cumulative evaporation up to 3500x for the overall experiment. The model evaporation went further than experimental evaporation to allow prediction past experimentally constrained evaporation limits. The evaporation model consisted of three steps:
- Speciation of the measured composition of the first sample at 95ºC suppressing all mineral precipitation in the calculation.
- Concentration/evaporation of the speciated water during stepwise addition of the starting solution speciated at 95ºC while allowing mineral precipitation.
- Correction of the predicted 95ºC pH values to 25ºC to compare to measured pH at room temperature in an additional simulation in which all mineral precipitation was suppressed.

For all calculations, electrical balance was achieved by automatically changing the sodium concentration with a convergence tolerance of 0.1ppb and the reaction pressure was allowed to vary by means of the 1.013-bar/steam-saturation curve. The model starting composition in leg 2 was based on the experimentally determined starting composition of leg 2. In some cases, minor mismatches between the experimental starting solution and the model calculations exist because of initial precipitation predicted by the model.

RESULTS

The results of the experimental evaporation studies are compared to those determined by thermodynamic modeling in Figure 1. Experimental results at 95ºC show that the carbonate-rich brine evolves towards a complex brine that contains about 99 mol% Na^+ for the cations, and 71 mol% Cl^-, 18 mol% $\Sigma CO_2(aq)$, 9 mol% SO_4^{2-} for the anions. The behavior of the evaporating, concentrating brine can be described through examination of both the experimental and model evaporation process. Modeling results shown in Figure 1 are obtained after mineral suppression and represent our best abilities to date to predict brine evolution.

It can be seen that sodium and chloride both concentrate conservatively during the evaporation process until the formation of a halite (NaCl) precipitate. This is a major factor in the evolution of potentially corrosive chloride, which may interact with the waste package in a repository environment. Potassium, nitrate and bromide also concentrate conservatively throughout the experimental and model evaporation process. The Pitzer parameter model is able to predict the behavior of sodium, potassium, nitrate, chloride and bromine, and the formation of halite at the end of the second leg. Sulfate concentrates in solution during the evaporation process until the formation of a thenardite (Na_2SO_4) precipitate. In leg 1, fluoride concentrates in solution until the formation of fluorite (CaF_2). Modeling results over-predicted fluoride solubility, possibly because of the lack of thermodynamic data on Kogarkoite ($Na_3(SO_4)F$), which was not identified by XRD in this study but has been observed by these investigators in similar experiments. In leg 2, the model, in contrast to experimental results, predicts no fluoride precipitation.

Magnesium was more difficult to model. The experimental plateau in magnesium concentration observed in leg 1 could only be modeled by the suppression of all magnesium silicate minerals. In contrast, leg 2 provided only one experimental value above the detection limit, which could only be modeled by allowing sepiolite ($Mg_4Si_6O_{15}(OH)_2 \cdot 6(H_2O)$) formation. This experimental value refers to the starting solution composition in leg 2 before any evaporation. Calcium was best modeled by allowing aragonite ($CaCO_3$) to precipitate from solution (as identified by XRD). Strontium concentrations decreased experimentally during leg 1, and modeling was unable to predict this trend with even when strontianite ($SrCO_3$) precipitation was allowed. Calcium and strontium were below the limits of detection at the end of leg 1 and therefore not included in the starting solution of leg 2. Modeling of aqueous carbonate and silica concentrations was poor in leg 1, but reasonable in the second leg, attributed to an inability to correctly model the experimental pH in leg 1. Any variation in pH and carbonate concentration may also impact the formation of strontianite, aragonite and amorphous silica. The discrepancy between experimental pH and corrected modeled pH is likely due to a difference in re-equilibration with CO_2 on cooling and pH measurement.
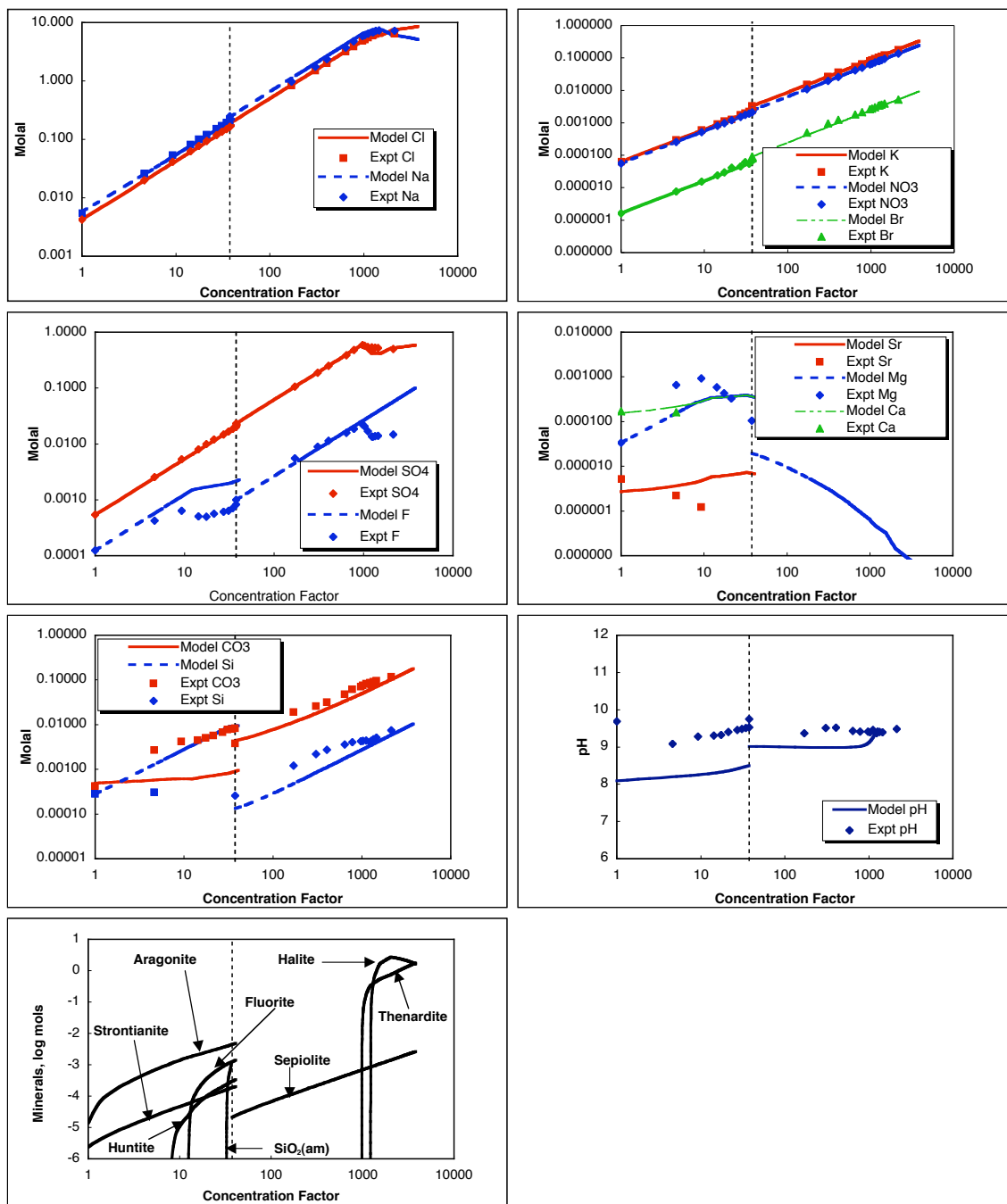
Figure 1. Evaporative evolution of carbonate-rich brines. Experimental solubilities (points), modeling predictions (solid and broken lines) and predicted mineral precipitation. Model pH values corrected to 25°C.

X-ray diffraction studies identified aragonite and halite in the first leg and halite, thenardite, burkeite ($Na_6(CO_3)(SO_4)_2$) and possibly a smectite clay formed in samples taken to dryness after the evaporation experiment. More investigation is needed to identify and characterize the possible smectite clay found. Strontianite, huntite ($CaMg_3(CO_3)_4$), fluorite, silica and sepiolite were not identified by XRD, although this may be due to their relative amounts

with respect to halite and thenardite in the final evaporated solution; XRD cannot detect amorphous solids or minerals that are present at < 2 wt %. This was supported by examining the modeled mass prediction for each mineral at the end of the evaporation process.

CONCLUSIONS

The experimental and modeled evaporation evolved to form the brine expected based on the starting composition. The important chemical divides that control the composition of brines formed from dilute carbonate type waters are halite, thenardite and aragonite and possibly magnesium silicate (sepiolite), amorphous silica, strontianite, huntite, fluorite and burkeite based on model predictions and experimental results. The precipitation of calcium as aragonite and magnesium as a magnesium silicate are important geochemical controls that prevent the formation of magnesium chloride and calcium chloride brines. Calcium and magnesium chloride brines are generally considered more corrosive than sodium chloride because of the higher solubility and higher boiling points of calcium chloride and magnesium chloride over halite. Additionally, calcium and magnesium chloride brines have a higher boiling point than a sodium chloride brine, and both calcium and magnesium hydrolyze, resulting in a lower pH than a sodium chloride brine. In most cases, the high temperature Pitzer parameter thermodynamic model used by Yucca Mountain researchers provides an adequate model of the experimental evaporative evolution. However, in the case of carbonate, magnesium silicate and strontium precipitates, preliminary modeling results are not an accurate reflection of experimental data due to lack of Pitzer parameters at elevated temperature, an incomplete thermodynamic dataset for potential mineral precipitation and a poor prediction of measured pH. The Pitzer interaction model was able to predict the evolution of the major brine-type, but was unable to adequately predict all relevant water chemistry evolution. More research is needed to validate the high temperature Pitzer interaction model using these experiments.

ACKNOWLEDGEMENTS

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